ADVANCED GEOCHEMISTRY OF NATURAL WATERS
GEOL 478/578
## Laboratory Exercise #5

Eh measurements

Eh is defined as the potential of a system relative to the potential of the standard hydrogen electrode (SHE). Eh is a notoriously difficult variable to measure in the field. It is common for a number of different redox couples, e.g., Fe^{2+}/Fe^{3+}, As^{3+}/As^{5+}, HS^-/SO_4^{2-}, to be out of equilibrium with each other and responding to apparently different Eh's. Nevertheless, Eh is normally measured and reported in most surveys of natural water compositions, and can, when used with caution, provide a relative indication of the redox conditions of a natural system. Higher Eh values correspond to more oxidizing conditions, lower Eh values correspond to more reducing conditions.

Eh is normally measured in the field using a Pt indicator electrode and a saturated calomel reference electrode (SCE). The Eh electrode is calibrated using a solution with known Eh. To convert Eh readings made in the field to true Eh values, i.e., vs. a SHE reference, one must add 244 mV to the reading made in the field. For more details on the definition, significance and measurement of Eh, refer Lecture 8 on the website: www.its.uidaho.edu/geol468_568.

a) Measure the potential of the Pt electrode in the reference ferricyanide/ferrocyanide solution. The reference should read 196 mV. The difference between 196 and the actual reading made should be added to every reading taken subsequently. It is not uncommon for the actual reading of the meter to differ by many tens of mV from the "true" Eh of the reference solution.

b) Measure the potential of the unknown buffer solution. Convert this reading to Eh vs. SCE, and Eh vs. SHE.

c) Try to obtain the Eh of a sample of tap water. Is it more difficult to get a stable reading compared to the buffers? If so, why?

Dissolved oxygen

Another means of obtaining information on the redox state of a natural water is to measure the dissolved oxygen concentration (usually reported in ppm or as % saturation). The dissolved oxygen concentration is related to Eh and pH via the following reaction and equation:

$$H_2O = 2H^+ + 1/2O_2(aq) + 2e^-$$
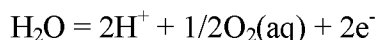
$$Eh = E^0 - 0.059 \, pH + 0.01475 \, \log [O_2]$$

We will use a dissolved oxygen meter and electrode to measure dissolved oxygen (DO) in tap water. Note that DO can be used as a measure of redox conditions only under relatively oxidizing conditions where the DO concentration is not too low to be detected by the meter and electrode (i.e., <0.1 ppm O_2).

Follow the instructions given for testing and calibrating the DO meter, and then measure DO in a sample of tap water.

Conductivity

Conductivity (or more correctly conductance) is the capacity of a solution to conduct an electric current and is measured in units of millisiemens per meter (mS m^{-1} = 10 μS cm^{-1} = 10 μmhos cm^{-1}). Conductivity provides a rough indication of the total number of ions present in a solution. It is hence related to Total Dissolved Solids (TDS) and ionic strength. TDS is defined as the total amount of solids (mg L^{-1}) remaining when a water sample is evaporated to dryness.

The exact relationship between TDS and conductivity can only be defined once the ionic composition is specified as conductivity depends on ionic charge and radius. However, in general, the relationship should be of the form:

$$\text{Conductivity (μS)} = \text{TDS (mg } L^{-1}) \times a$$

where a = 1.2-1.8. The above relationship can be used as a quality control criterion for water quality analyses.

After being instructed in the use of the conductivity meter, determine the conductivity of DI water and tap water.